13

ON THE HEAT CAPACITIES OF A FEW CRYSTALS AT LOW TEMPERATURES

By S. C. SIRKAR

AND

J. GUPTA.

(*Received for publication, April 25, 1938.*)

ABSTRACT. The heat capacities of crystals of ammonium chloride, carbon dioxide, sulphur and benzene observed at low temperatures have been examined in order to ascertain whether the observed values of C_v indicate the presence of the contributions of Debye functions corresponding to the new Raman lines in the low frequency region observed with these crystals. It has been found that in the case of ammonium chloride a Debye function corresponding to the line 183 cm^{-1}, and another Einstein function for the angular oscillations can explain satisfactorily the values of C_v observed at low temperatures. In the case of carbon dioxide and sulphur on the other hand, Einstein functions corresponding to the new lines, instead of Debye functions have to be taken into account in order to explain the observed values of C_v. In the case of benzene also, there is agreement between the observed and the calculated values of C_v if the Einstein functions corresponding to the new lines are taken into consideration. It is pointed out that the above fact as well as the selection rules for the appearance of Raman lines due to lattice oscillations, when applied to the crystals of benzene definitely lead to the conclusion that the new lines are not due to lattice oscillations in the case of benzene.

It is well known that the heat capacities of many crystals at low temperatures are not given by a Debye function alone even when the contributions of the Einstein functions due to the known intramolecular vibrations are quite negligible. It was pointed out by Pauling[1] that simple molecules, *e.g.*, N_2, O_2, H_2, CO, HCl, HBr, etc., execute angular oscillations about equilibrium orientations even at very low temperatures, and in some cases the molecules rotate freely in the solid state above some critical temperatures. As the frequencies of such oscillations are low, the corresponding Einstein functions contribute appreciably to the heat capacities at low temperatures, besides the Debye functions. The contribution of the Debye function to C_v can be easily calculated if the frequency of lattice oscillation be known. In the case of the substances mentioned above the frequencies of lattice oscillation were not known and therefore Pauling tried to calculate the values of ν, the frequencies of angular oscillation by assuming that the temperature at which the heat capacity reduces to 5 cal./mole.

per degree is equal to $\frac{h\nu}{3k}$ and the separate contributions of Debye and Einstein functions could not be calculated more accurately. In recent years, the study of the Raman spectra of solid substances having molecules more complicated than those discussed by Pauling has revealed the presence of new Raman lines with values of $\Delta\nu$ ranging from about 20 cm^{-1} up to about 190 cm^{-1}. Gross and Vuks[2] who first observed these new lines in the case of a few aromatic compounds suggested that the lines might be due to lattice oscillations. Such lines were observed by one of the present authors[3] in the case of many substances in the solid state and at the temperature of liquid oxygen and those investigations have since been extended to a few organic and inorganic compounds by the present authors.[4] It has also been pointed out by one of the present authors[5] that strong new lines are observed in some cases even when lattice oscillations are forbidden in Raman effect according to selection rules. Recently, Venkateswaran[6] has suggested that flexural oscillations of the lattice are responsible for the origin of the new Raman lines. Since the oscillations of different molecules have definite phase relations in the case of the flexural oscillation postulated by Venkateswaran, this oscillation is different from the angular oscillations of individual molecules postulated by Pauling, and should be treated as a lattice oscillation when its contribution to the heat capacity is considered. The object of the present paper is to discuss how far the observed heat capacities at low temperatures are explained by assuming that the new lines are due either to ordinary lattice oscillations or to the flexural oscillations of the lattice mentioned above.

AMMONIUM CHLORIDE

It may be of interest first to examine whether there is quantitative agreement between the observed heat capacities and those calculated in the case of the crystals for which the frequency of lattice oscillation is known. The crystals of ammonium chloride furnish a suitable example to be dealt with for this purpose, because it has been shown by Menzies and Mills[7] by investigating the Raman spectra of these crystals, that the new line at 183 cm^{-1} which appears at temperatures below $-30°C$ is due to lattice oscillation. It has already been pointed out by Pauling[8] that since there is a catastrophic change in the heat capacity at about $-30°C$, probably the ammonium ions begin to rotate freely at this temperature and therefore at lower temperatures they are executing angular oscillations of small amplitudes about equilibrium orientations. These oscillations do not produce any appreciable change in polarisability in an isotropic ion like NH_4^+, and so the Raman lines due to these oscillations are not observed. Also it has been shown by Menzies and Mills conclusively that the new line at 183 cm^{-1} is due to the oscillation of the lattice through the NH_4 ions against that through the Cl ions. The crystals

being cubic, the frequency of lattice oscillation is the same for all the three degrees of freedom and for the tetrahedral ammonium ion, the angular oscillation can also take place about all the three axes with the same frequency. The heat capacities are expected in this case to be given by the relation $C_v = 3RD(\theta/T) + 3RE(\theta'/T)$, where θ and θ' are respectively equal to $h\nu/k$ and $h\nu'/k$, ν and ν' being the frequencies of lattice and angular oscillations respectively. In this case ν may be assumed to be equal to 180 cm^{-1}, because though Menzies and Mills have observed that the frequency of this line does not alter appreciably with the lowering of temperature, it is expected to increase by 2 or 3 cm^{-1} at very low temperatures. The values of ν' is not known. It can be assumed however that at very low temperatures $3RE(\theta'/T) = C_v - 3RD(\theta/T)$ and if with the value of ν' calculated in this way for a particular temperature, the values of C_v calculated for other temperatures agree with the observed values, it may be concluded that the value of ν' so obtained is not far from the actual value. The calculated values of C_v with the assumption that $\theta = 266°5$ and $\theta' = 190°$ are given in table I. It will be seen that there is fair agreement between these values and the observed values[9] of C_p given in the last column up to 125° K.

TABLE I. NH_4Cl. $\theta = 266°5$, $\theta' = 190°$.

T	$3RD(\theta/T)$	$3RE(\theta'/T)$	$3RD(\theta/T) + 3RE(\theta'/T)$	C_p observed.
23	0·295	0·106	0·40	·525
48	1·85	1·85	3·70	3·42
73	3·31	3·49	6·80	6·48
125	1·77	1·90	0·67	10·52

At higher temperatures, however, the observed values of C_p are higher than the calculated values of C_v. This is probably due to the fact that $C_p - C_v$ has appreciable values at these temperatures.

It is quite evident from the example of NH_4Cl discussed above that when the frequency of lattice oscillation is known, the contribution of the corresponding Debye function is less than the observed value of C_p, if the angular oscillations postulated by Pauling are also present. The heat capacities of a few other crystals with which new Raman lines have been observed in the low frequency region can be examined now from the point of view mentioned above.

CARBON DIOXIDE

It has been observed recently by the present authors[10] that a new Raman line with $\Delta\nu$ equal to 58 cm^{-1} appears in the Raman spectrum of solid carbon

dioxide at about $-80°C$. It was also pointed out that as the Raman lines due to lattice oscillation involving translational motions of the molecules are forbidden in this case according to selection rules, the new line is not due to a lattice oscillation but may be due to an intermolecular oscillation in groups of molecules, there being weak electronic binding between different molecules in each group. As in this case the heat capacities at low temperatures are known, it can be easily ascertained whether the values of C_v at low temperatures are given by a Debye function corresponding to the observed frequency mentioned above. Since it has been observed in the case of a few organic crystals that the values of $\Delta\nu$ of the new Raman lines in the low frequency region increase by 5 to 10% on cooling the crystal from room temperature up to about $-180°C$, it may be assumed that the value of $\Delta\nu$ of the new line of solid carbon dioxide increases to about 03 cm^{-1} at low temperatures. Then $\theta = h\nu/k = 90°\cdot3$. Also θ has the same value for all the three degrees of freedom, because the crystal belongs to the cubic system. The calculated values of $3RD(\theta/T)$ for the three degrees of freedom are given in column 2 of table II. It can be seen that these values are much larger than the observed values[11] of C_v given in the last column. Hence the new Raman line

TABLE II.

CARBON DIOXIDE.

(1) T	(2) $3RD(\theta/T)$ $\theta = 90°\cdot3$	(3) $3RE(\theta/T)$ $(\theta = 90°\cdot3)$	(4) $3RE(\theta/T)$ $\theta = 90°\cdot3$	(5) $3RD(\theta'/T)$ $(\theta' = 150°)$	(6) $3RE(\theta''/T)$ $(\theta'' = 200°)$	(7) C_v Calc ; Col (1) + Col(5) + Col(6)	(8) C_v obs.
15·5	1·09	·40	·10	·50	·00	·60	·61
19·1	2·13	·80	·20	·87	·01	1·08	1·08
25·6	3·43	1·52	·38	1·66	·10	2·14	2·27
30·0	4·15	2·10	·60	2·85	·47	3·92	4·06
47·6	5·01	2·90	·71	3·80	1·08	5·02	5·79
56·2	5·20	3·21	·81	4·28	1·49	6·58	6·77
61·3	5·34	3·32	·83	4·50	1·75	7·08	7·30
81·9	5·61	3·60	·90	5·07	2·47	8·44	8·70
97·9	5·71	3·62	·92	5·32	2·83	9·07	9·42

cannot be due to a lattice oscillation either translational or flexural, the latter involving translational as well as angular oscillation of the molecules about equilibrium orientation as postulated by Venkateswaran. Again, if the new line were due to the angular oscillations of the individual molecules about equilibrium orientation, its contribution to C_v would be $2\,R\,E\,(\theta/T)$, because there are two

degrees of freedom for rotation about two axes perpendicular to the axis of the molecule. The values of $2\ R\ E\ (\theta/T)$ are given in column 3 of table II. It can be seen that the contributions of another Debye function with three degrees of freedom, which are to be added to the above values of $2\ R\ E\ (\theta/T)$ in order to get the values of C_v, become very small, and this is absurd. Hence the new line cannot be due to the angular oscillations. There is another reason for coming to this conclusion. It has been pointed out by Pauling that the amplitude of the angular oscillation diminishes with lowering of temperature and as the intensity of the corresponding Raman line depends on the amplitude, the intensity ought to diminish at low temperatures, if the line be due to angular oscillations. This remark is true also for the flexural oscillation postulated by Venkateswaran. Though the Raman spectrum of solid carbon dioxide has not been studied at temperatures lower than $-80°$ C, it has been observed in the case of benzene, diphenyl ether, *p*-dichlorobenzene and *p*-dibromobenzene that there is no diminution in the intensity of the new lines with the lowering of temperature. Hence in those cases the new lines are not due to angular oscillations of the molecules, and the same may be true also in the case of carbon dioxide.

On the other hand, the contributions of $\frac{R}{2}\ E\ (\theta/T) + 2\ R\ E(\theta''/T)$ together with that of $3\ R\ D(\theta'/T)$ with θ' 150° and θ'' equal to 200° agree fairly well with the observed values of C_p at the low temperatures. It is difficult to interpret this result but it may mean that as the new line contributes only $\frac{R}{2}\ E\ (\theta/T)$ to C_v, it may be due to an ordinary oscillation with one degree of freedom resembling an intramolecular oscillation in a diatomic molecule, because in that case each carbon dioxide molecule as a whole would play the part of an atom and the contribution to C_v per mole. would be $\frac{R}{2}\ E\ (\theta/T)$ for the particular oscillation. It is also indicated by the above results that the frequency of lattice oscillation in the case of solid carbon dioxide is much larger than 58 cm^{-1}. It can be seen from table II that the calculated values of C_v are slightly less than the observed values of C_p at higher temperatures. This is probably due to the fact that $C_p - C_v$ may have appreciable values at these temperatures, because $C_p - C_v$ may be roughly equal to 0·0214. $\frac{T}{T_s} . C_p^2$, T_s being the melting point.

SULPHUR

Sulphur is known to exist as S_8 molecules even in solutions and the Raman lines 150, 216, 434 and 470 cm^{-1} are observed.[12] The orthorhombic crystals of sulphur, however, give a few more Raman lines besides the above lines. The

lines observed by Venkateswaran[13] are 85, 103, 154, 183, 218, 245, 432 and 472 cm^{-1}. Of these the line 103 cm^{-1} was not observed by Krishnamurti, but since this frequency as well as another less than 77 cm^{-1} are observed in the infra-red, their contributions are also to be taken into consideration while calculating the heat capacities of sulphur. The line 85 cm^{-1} was supposed to be due to the vibration of S_{16} molecule by Krishnamurti and this view was also held by the present authors[15] who observed that this line remains in the same position even at the temperature of liquid oxygen. Venkateswaran has pointed out on the other hand, that this line is due to a lattice oscillation. The correctness of this latter hypothesis can be tested by examining the observed heat capacities of sulphur at low temperatures. If for simplicity we assume that the lattice oscillation has the same frequency 84 cm^{-1} for all the three degrees of freedom, the heat capacities ought to indicate the presence of the contribution of a Debye function, 3 R D (θ/T) with three degrees of freedom and with θ equal to 120°. The calculated values of 3 R D (θ/T) are given in column 2 of table III and the observed values of C_p per gram-atom [16] per degree are given in column 3.

TABLE III.

SULPHUR.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
T	$3RD\left(\frac{\theta}{T}\right)$ $(\theta = 120°)$	C_p obs. per gm-atom per degree	C_p obs per mole per degree	$3RD\left(\frac{\theta'}{T}\right)$ $\theta' = 47°$	$R\sum_1^3 E\left(\frac{\theta_n}{T}\right)$	$3RD\left(\frac{\theta'}{T}\right) + R\sum_1^3 E\left(\frac{\theta_n}{T}\right)$	(7) $-C_p$ obs.
10	0·207	0·31	2·48	2·42	0·01	2·43	0·05
20	1·582	0·72	5·71	4·59	0·60	5·19	0·55
30	2·906	1·15	9·18	5·30	1·88	7·18	2·0
40	3·948	1·46	11·67	5·54	3·38	8·92	2·75
50	4·51	1·77	14·16	5·69	4·62	10·31	3·85
60	4·92	2·07	16·60	5·78	5·78	11·56	5·04
70	5·18	2·37	18·94	5·84	6·70	12·54	6·4

It can be easily seen that the observed values of C_p do not follow a Debye curve at all. Hence the line 84 cm^{-1} cannot be due to lattice oscillation, because the calculated value of 3 R D (θ/T) with θ equal to 120° coincides with C_p observed at 10°K, but the calculated values are many times larger than the observed values at higher temperatures. Next, let us deal with S_8 molecules and compare

the calculated values with observed values of C_p for the S_8 molecule. The observed values are given in column 4. The contribution to C_p of any Einstein function with θ greater than 40° is very small at 10° K, and therefore the value of C_p observed at this temperature determines the Debye function which is actually responsible for almost the whole of C_p. It can be seen from column 5 that a Debye function with three degrees of freedom and with θ equal to 47° is responsible for the values of C_p for S_8 at the low temperatures. The contribution of any intramolecular oscillation of frequency ν_n to C_p is $R\mathrm{E}(\theta_n/T)$ where the Einstein function has one degree of freedom. The values of $R\Sigma\mathrm{E}(\theta_n/T)$ are given in column 6. Only six frequencies have been considered so that θ_1, θ_2, θ_3, θ_4, θ_5 and θ_6 are respectively equal to 100°, 120°, 147°, 220°, 295°, and 303°. The values of $3R\mathrm{D}(\theta'/T) + R\Sigma\mathrm{E}(\theta_n/T)$ are given in column 7. It can be seen from column 8 that the balances $C_p - \{3R\mathrm{D}(\theta'/T) + R\Sigma\mathrm{E}(\theta_n/T)\}$ follow an Einstein curve. Hence these are contributions of some other Einstein functions corresponding to some intramolecular oscillations which have not been recorded either in the infra-red or in the Raman spectra.

Thus it is evident that the line 84 cm^{-1} behaves as an intramolecular oscillation. Actually, however, it is not due to an oscillation in a S_8 molecule, because the line is absent in the case of solutions containing S_8 molecules. The above difficulty may be overcome by assuming that pairs of S_8 molecules are present in the crystals so that two molecules in each pair are bound to each other only by a weak electronic binding and that the line 84 cm^{-1} is due to the oscillation of the two S_8 molecules against each other. In order to calculate the value of C_p, however, it is enough to consider the S_8 molecule, and to take into consideration only half the contribution of the corresponding θ_n. If that would be done, the balances in the last column would be larger, but would still follow an Einstein curve. If the frequency of the lattice oscillations were known more definitely, it could be decided whether the molecules is S_8 or S_{16} in the solid state, but the above discussions lead to the definite conclusion that the observed heat capacities of sulphur at low temperatures cannot be explained by assuming the line 84 cm^{-1} to be due to a lattice oscillation.

BENZENE

In the case of solid benzene just below the melting point, two new Raman lines at 63 cm^{-1} and 108 cm^{-1} were observed by Gross and Vuks [17] and at the temperature of liquid oxygen three lines at 81 cm^{-1}, 98 cm^{-1} and 124 cm^{-1} were observed by one of the present authors.[18] The lines are observed to be sharp at the lower temperature and their intensities do not diminish at the lower temperature. The crystals of benzene belong to the space group V_h^5 with four molecules per unit cell,[19] the molecule itself being centrosymmetrical. If the centres of the four molecules be at 000, ½ ½ 0, ½ 0 ½ and 0 ½ ½, each of these points also becomes

centre of symmetry of the distribution of matter around it. Hence according to selection rules mentioned in previous sections the Raman lines due to vibration of the lattice through one set of molecules against that through any other set are forbidden in this case. It can be therefore assumed that these new lines are not due to lattice oscillation in this case. Also, since the intensity of the lines does not diminish even at -180°C these lines cannot be due either to angular oscillation postulated by Pauling or to the flexural oscillation suggested by Venkateswaran and referred to in the previous sections. If the lines were due to lattice oscillation, their contribution to C_v would be $R\sum_{1}^{3} D(\theta_n/T)$ where $\theta_1 = 116.1^{\circ}$, $\theta_2 = 140^{\circ}.5$ and $\theta_3 = 177^{\circ}.7$. These values are given in column 2 of table IV. It can be seen by comparing these values with the observed values[20] of C_p, that the calculated values are much less than the observed values. If the corresponding Einstein functions are calculated, the values of C_v given in column 3 are obtained. These values together with the contribution of a Debye function with θ' equal to $121^{\circ}.5$ and with three degrees of freedom agree with the observed values of C_p up to about 70°K and at higher temperatures the observed values become larger than the calculated values. Since at temperature higher than 90°K, the values of C_p exceed 12 cal./mole/degree, it is evident that besides the above Einstein and Debye functions other Einstein functions are also contributing to C_v at these temperatures Recently, Lord, Ahlberg and Andrews[21] have discussed the heat capacities of benzene at low temperatures but they

TABLE IV.

Benzene.

τ	$R\sum_{1}^{5} D\left(\frac{\theta_n}{T}\right)$	$R\sum_{1}^{3} E\ \frac{\theta_n}{T}$	$3RD\left(\frac{\theta'}{T}\right)$	C_v Calc. (col. 3 + col 4)	C_p obs.
4	0·009	0·00	0·017	0·017	0·0195
8	0·094	0·00	0·132	0·132	0·147
10	0·159	0·003	0·26	0·263	0·346
20	1·14	0·31	1·54	1·85	1·84
30	2·39	1·25	2·95	4·20	4·24
40	3·37	2·28	3·91	6·19	6·47
50	4·06	3·12	4·51	7·63	8·14
60	4·52	3·74	4·09	8·63	9·32
70	4·85	4·21	5·14	9·35	10·16

have not taken into consideration the frequencies of the new Raman lines observed in the low frequency region. On the other hand, they have, assumed that the heat capacities at low temperatures are given by $6RD(\theta/T)$ with θ equal to 150°, where $3RD(\theta/T)$ is for the contribution of translational oscillations of the lattice and the remaining half for that of the ocillation involving a definite phase relation among the angular oscillations of different molecules. They have thus assumed that practically there are two Debye functions instead of one, effective at low temperatures. It has already been concluded from the considerations of the observed intensity of the new Raman lines that the new lines may not be due to any of the two lattice oscillations mentioned above. Therefore the Einstein functions corresponding to these lines are to be taken into consideration. Table IV shows that there is agreement between observed and calculated heat capacities between 4° K and 70° K taking those Einstein functions and one Debye function with $\theta' = 121°.5$. Now it can be seen from table V that at higher temperatures also, there is agreement between observed and calculated values of C_p if the values of $C_p - C_v$ and the contributions $R\Sigma E(\theta_n/T)$ of internal frequencies of the benzene molecule are taken into consideration. Contribution of the latter Einstein functions as well as the values of $C_p - C_v$ have been calculated by the authors mentioned above and these have been used here. The calculated and observed values are given in table V. Results only up to 130° K have been given because it is evident that if there be agreement between the

TABLE V.

Benzene.

T	$R\sum_1^3 E\left(\frac{\theta_n}{T}\right)$	$3RD\left(\frac{\theta'}{T}\right)$ $\theta' = 121{\cdot}5$	$R\Sigma E\left(\frac{\theta'_n}{T}\right)$	$C_p - C_v$	C_p Calc.	C_p obs.
80	4·55	5 32	0·17	0·54	10·58	10·15
90	4·81	5·44	0·31	0·67	11·23	11·44
100	4·99	5·54	0·51	0·81	11·85	11·99
110	5·15	5·61	0·79	0·97	12·52	12.59
120	5·25	5·66	1.09	1·13	13·13	13·24
130	5·37	5·70	1·45	1·33	13·85	13·96

observed and calculated values up to this temperature, at higher temperatures also there will be agreement.

Thus it is evident that the heat capacities of benzene at low temperatures can be explained without assuming the new lines to be due to lattice oscillations, and in view of the fact that selection rules do not allow the lattice oscillations to appear in the Raman effect, it seems that the calculated value of C_v given in column 5 of table IV, are more reliable than those obtained with the assumption that the new lines are due to lattice oscillations.

Since with *p*-dichlorobenzene, naphthalane and *p*-dibromobenzene, new lines with very small values of $\Delta\nu$ are observed, the values of C_v at low temperatures ought to be very high if these lines be due to lattice oscillations. But data for sufficiently low temperatures are not available and therefore the calculation of C_v has not been possible in these cases.

PALIT LABORATORY OF PHYSICS,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

REFERENCES.

[1] Pauling, L., *Phys. Rev.*, **36**, 430 (1930).

[2] Gross, E. and Vuks, M., *Nature*, **135**, 100, 431 and 998 (1935).

[3] Sirkar, S. C., *Ind. J. Phys.*, **10**, 109 (1935); *Ibid*, 189 (1936).

[4] Sirkar, S. C. and Gupta, J., *Ind. J. Phys.*, **10**, 227 (1936); *Ibid*, **10**, 473 (1936); *Ibid*, **11**, 55 (1937); *Ibid*, **12**, 35 (1938).

[5] Sirkar, S. C., *Ind. J. Phys.*, **11**, 343 (1937).

[6] Venkateswaran, C. S., *Curr. Sci.*, **6**, 378 (1938).

[7] Menzies, A. C., and Mills, H. R., *Proc. Roy. Soc. A*, **148**, 407 (1935).

[8] *Loc. cit.*

[9] *International Critical Tables*, **5**, p. 95.

[10] Sirkar, S. C., and Gupta, J., *Curr. Sci.*, **6**, 214 (1937).

[11] *International Critical Tables*, **5**, p. 86; also *cf.* Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[12] Krishnamurti, P., *Ind. J. Phys.*, **5**, 105 and 587 (1935).

[13] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, **4**, 345 (1936).

[14] Barnes, R. B., *Phys. Rev.*, **39**, 562 (1932).

[15] Sirkar, S. C. and Gupta, J., *Ind. J. Phys.*, **10**, 473 (1936).

[16] *International Critical Tables*, **5**, p. 85.

[17] *Loc. cit.*

[18] Sirkar, S. C., *Ind. J. Phys.*, **10**, 189 (1936).

[19] Wyckoff, *The Structure of Crystals*, 1931, p. 385.

[20] Ahlberg, J. E., Blanchard, E. R. and Lundberg, W. O., *J. Chem. Phys.*, **5**, 539 (1937).

[21] Lord, R. C., Ahlberg, J. E. and Andrews, D. H., *J. Chem. Phys.*, **5**, 649 (1037).